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(54) Title: A PROCESS FOR MAKING PAPER			
(57) Abstract  The invention relates to a process for making paper wherein an anionic starch, which is based on a starch comprising at least 95 wt.%, based on dry substance of the starch, of amylopectin, or a derivative of said starch, is used in combination with a fixative as a strengthening agent.			

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Title: A process for making paper

The invention relates to a process for making paper and to the use of starch in said process.

In order to increase the strength properties of paper, it has been common practice during the last thirty  
5 years to add cationic starch at the wet-end stage of the papermaking process. The wet-end of the papermaking process refers to the stages of the papermaking process, wherein a pulp of fibers, obtained from cellulose-based materials, such as recycled, used paper, wood, cotton, or alternative  
10 sources, is being processed. The term "wet-end" originates in the large amounts of water, in the presence of which the pulp is processed.

During the last decade, there have been several trends in the papermaking process which either call for more  
15 starch in the paper than is feasible with cationic starch, or which make the application of cationic starch more difficult. One of these trends is the environmental demand to recycle paper. As paper is recycled, the fibers of the paper tend to become shorter and weaker, the latter of which is due to  
20 reduced interactions among the fibers. As a result, increased amounts of starch are necessary in the wet-end of the papermaking in order to produce a paper which is sufficiently strong. It has been found that after paper has been recycled a certain number of times, the loss of strength due to  
25 recycling cannot be compensated by adding cationic starch, leading to paper having an inferior paper strength.

Another trend is the urge to produce cheaper paper. This can be achieved by incorporating large amounts of a  
cheap filler into the paper. However, a larger filler content  
30 of the paper results in a deterioration of paper strength, which gives rise to a demand for the addition of increased amounts of starch in the wet-end.

Yet another trend concerns a change in the apparatuses used in the papermaking process. The  
35 conventionally used size-press is more and more being

replaced by a premetering size-press. The use of a premetering size-press often has the effect that starch penetrates to lesser degree into the paper sheet than when a conventional size-press is used. As a result, the starch provides a smaller contribution to the strength of the paper. Moreover, the use of a premetering size-press for pigmentizing diminishes the internal strength of the paper even more. Therefore, it is desired to provide an increase of the strength of the paper obtained in the wet-end.

In "Anionic starch: an effective wet-end concept for enhancing paper strength", Proceedings of the PITA Annual Conference, 87-91, Manchester, October 1997, J. Terpstra and R.P. Versluijs have proposed to use anionic starch instead of cationic starch as a strengthening agent in the wet-end of the papermaking process, in order to achieve a greater internal strength of the paper produced. This concept of using anionic starch has also been described in P. Brouwer, Wochenblatt für Papierfabrikation, 19 (1997), 928-937, WO-A-93/01353 and WO-A-96/05373, and may be explained as follows.

The fibers and filler particles, which are used to produce paper from, are negatively charged. When cationic starch is used as a paper strengthening agent, its retention is mainly caused by the interaction between the positively charged starch and the negatively charged fibers and filler particles. In order to adhere anionic starch molecules onto anionic fibers and filler particles, use is made of a so-called cationic fixative. In principle, any cationic paper aid can be used as a fixative for the anionic starch, although some lead to better results than others. Because they are cheap and hardly affected by water hardness, polyaluminum chlorides are considered very attractive fixatives. Other materials that have been proposed for use as a fixative in this regard are, inter alia, alum, or cationic polymers, such as polydimethyldiallylammonium chloride and polyamines.

It has been found that, by using anionic starch in combination with a suitable fixative, it is possible to incorporate up to five times as much starch into a paper sheet in comparison with the case wherein only cationic starch is used as a strengthening agent. Of course, this results in a much stronger paper sheet. At the same time, the retention of the starch in a papermaking process is much higher when anionic starch and a fixative are used instead of cationic starch. This means, that a much smaller part of the starch, which is added to the pulp in the wet-end of the papermaking process, is lost to the processing water. Furthermore, by using anionic starch in combination with a suitable fixative, it has been found that the retention of fines and fillers is increased substantially, and it is possible to reduce the refining. Also, an increase in dewatering speed has been observed.

A disadvantage of the use of anionic starch instead of cationic starch in the wet-end of the papermaking process resides in the necessity of using a fixative. Even though some of the fixatives proposed in the art are relatively cheap, the costs of the paper that is produced may increase considerably because of the use of the fixative. Also, as the fixative is a cationic compound, it is inevitable that anionic counterions are added to the paper along with the fixative. Often, the counterions are chloride ions which are corrosive. Furthermore, the use of a fixative may lead to a hardening of the process water and to the production of salts, which may interfere with other papermaking aids.

Surprisingly, it has now been found that the above described disadvantages of the use of anionic starch as a strengthening agent in paper may be mitigated by using an anionic starch which primarily comprises amylopectin.

Hence, the invention relates to a process for making paper wherein an anionic starch, which is based on a starch comprising at least 95 wt.%, based on dry substance of the

starch, of amylopectin, or a derivative of said starch, is used in combination with a fixative as a strengthening agent.

The use of the specific anionic starch has been found to make it possible to use significantly smaller amounts of a fixative, when compared with the use of a conventional anionic starch. Moreover, the incorporation of an anionic starch which primarily comprises amylopectin into a paper sheet leads to a paper sheet having a superior strength.

Most starch types consist of granules in which two types of glucose polymers are present. These are amylose (15-35 wt.% on dry substance) and amylopectin (65-85 wt.% on dry substance). Amylose consists of unbranched or slightly branched molecules having an average degree of polymerization of 1000 to 5000, depending on the starch type. Amylopectin consists of very large, highly branched molecules having an average degree of polymerization of 1,000,000 or more. The commercially most important starch types (maize starch, potato starch, wheat starch and tapioca starch) contain 15 to 30 wt.% amylose.

Of some cereal types, such as barley, maize, millet, wheat, milo, rice and sorghum, there are varieties of which the starch granules nearly completely consist of amylopectin. Calculated as weight percent on dry substance, these starch granules contain more than 95%, and usually more than 98% amylopectin. The amylose content of these cereal starch granules is thus less than 5%, and usually less than 2%. The above cereal varieties are also referred to as waxy cereal grains, and the amylopectin-starch granules isolated therefrom as waxy cereal starches.

In contrast to the situation of different cereals, root and tuber varieties of which the starch granules nearly exclusively consist of amylopectin are not known in nature. For instance, potato starch granules isolated from potato tubers usually contain about 20% amylose and 80% amylopectin (wt.% on dry substance). During the past 10 years, however, successful efforts have been made to cultivate by genetic

modification potato plants which, in the potato tubers, form starch granules consisting for more than 95 wt.% (on dry substance) of amylopectin. It has even been found feasible to produce potato tubers comprising substantially only amylopectin.

In the formation of starch granules, different enzymes are catalytically active. Of these enzymes, the granule-bound starch synthase (GBSS) is involved in the formation of amylose. The presence of the GBSS enzyme depends on the activity of genes encoding for said GBSS enzyme. Elimination or inhibition of the expression of these specific genes results in the production of the GBSS enzyme being prevented or limited. The elimination of these genes can be realized by genetic modification of potato plant material or by recessive mutation. An example thereof is the amylose-free mutant of the potato (amf) of which the starch substantially only contains amylopectin through a recessive mutation in the GBSS gene. This mutation technique is described in, inter alia, J.H.M. Hovenkamp-Hermelink et al., "Isolation of amylose-free starch mutant of the potato (*Solanum tuberosum* L.)", Theor. Appl. Genet., (1987), 75:217-221, and E. Jacobsen et al., "Introduction of an amylose-free (amf) mutant into breeding of cultivated potato, *Solanum tuberosum* L.", Euphytica, (1991), 53:247-253.

Elimination or inhibition of the expression of the GBSS gene in the potato is also possible by using so-called antisense inhibition. This genetic modification of the potato is described in R.G.F. Visser et al., "Inhibition of the expression of the gene for granule-bound starch synthase in potato by antisense constructs", Mol. Gen. Genet., (1991), 225:289-296.

By using genetic modification, it has been found possible to cultivate and breed roots and tubers, for instance potato, yam, or cassave (Patent South Africa 97/4383), of which the starch granules contain little or no amylose. As referred to herein, amylopectin-potato starch is

the potato starch granules isolated from potato tubers and having an amylopectin content of at least 95 wt.% based on dry substance.

Regarding production possibilities and properties, there are significant differences between amylopectin-potato starch on the one hand, and the waxy cereal starches on the other hand. This particularly applies to waxy maize starch, which is commercially by far the most important waxy cereal starch. The cultivation of waxy maize, suitable for the production of waxy maize starch is not commercially feasible in countries having a cold or temperate climate, such as The Netherlands, Belgium, England, Germany, Poland, Sweden and Denmark. The climate in these countries, however, is suitable for the cultivation of potatoes. Tapioca starch, obtained from cassave, may be produced in countries having a warm climate, such as is found in regions of South East Asia and South America.

The composition and properties of root and tuber starch, such as amylopectin-potato starch and amylopectin-tapioca starch, differ from those of the waxy cereal starches. Amylopectin-potato starch has a much lower content of lipids and proteins than the waxy cereal starches. Problems regarding odor and foaming, which, because of the lipids and/or proteins, may occur when using waxy cereal starch products (native and modified), do not occur, or occur to a much lesser degree when using corresponding amylopectin-potato starch products. In contrast to the waxy cereal starches, amylopectin-potato starch contains chemically bound phosphate groups. As a result, amylopectin-potato starch products in a dissolved state have a distinct polyelectrolyte character.

The invention contemplates the use of anionic starch obtained from cereal and fruit sources on the one hand, and root and tuber sources on the other hand. Of the cereal starches, waxy maize starch has proven very suitable. In general, however, root and tuber starches are more preferred.



As has been indicated above, it is often advantageous to use a starch having a very low content of lipids and/or proteins. The use of anionic amylopectin-potato starch and amylopectin-tapioca starch as a strengthening agent in paper has been found to lead to a particularly strong paper sheet.

By the term anionic starch is meant a starch having a charge density of at least 0.03  $\mu\text{eq}/\text{mg}$  starch, preferably at least 0.15  $\mu\text{eq}/\text{mg}$  starch. In the context of the invention, the charge density is defined as the amount of a cationic polymer (methyl glycol chitosan iodide, Sigma M-3150) which has to be added to a known amount of dissolved starch in order to reach the equivalence point. This equivalence point may be determined by measuring the electrophoretic zetapotential of the dispersion to which silicate particles are added as indicator. The zetapotential can for instance be measured by using a Malvern Zetasizer 3.

The anionic starch, which, according to the invention, is used in combination with a fixative as a strengthening agent in paper, may be prepared from the starch comprising at least 95 wt.%, based on dry substance of the starch, of amylopectin, or the derivative of said starch, on which it is based in any manner known for regular starch comprising both amylopectin and amylose. For a description of a possible manner of preparing an anionic starch, reference may be made to O.B. Wurzburg (Ed.), "Modified Starches: Properties and Uses", CRC Press Inc., Boca Eaton, Florida, 1986.

Examples of anionic starch may be obtained by introduction of any anionic substituents or by any oxidation process known in the derivatization of starch. Suitable examples of anionic substituents are phosphate, phosphonate, sulfonate, sulfate, (alkyl)succinate, anionic graft copolymers and combinations thereof. An example of a suitable oxidation is oxidation by hypochlorite. Preferably, a carboxymethyl or phosphated starch is used. The degree of substitution (DS), which is the molar ratio between the

amount of substituted hydroxyl groups of a glucose unit in the starch and the amount of glucose units in the starch, may range between 0.005 and 0.5, preferably between 0.01 and 0.2, more preferably between 0.01 and 0.1.

5           Suitable derivatives of a starch comprising at least 95 wt.% amylopectin (based on dry substance) are starches wherein, besides an anionic substituent, also one or more non-ionic or cationic substituents may be introduced. Suitable examples of non-ionic or cationic substituents may  
10 be introduced by etherification idem esterification reactions, such as methylation, ethylation, hydroxyethylation, hydroxypropylation, alkylglycidylation (wherein the length of the alkyl chain varies from 1 to 20 carbon atoms), acetylation, propylation, carba-imidation, diethylamino-  
15 ethylation, and/or trimethylammoniumhydroxypropylation. Further, the starch may be crosslinked by any crosslinking known in the derivatization of starch. Examples of suitable crosslinking agents include epichlorohydrine,  
20 dichloropropanol, sodium trimetaphosphate, phosphorousoxychloride and adipic acid anhydride. Of course, care should be taken that the overall charge of the starch is anionic.

As has been indicated hereinabove, it is essential to use a fixative, when anionic starch is used in the wet-end to  
25 provide strength in paper. In accordance with the invention, suitable fixatives are cationically charged compounds, which are capable of binding anionic starch to anionic paper fibers and filler particles. In principle, any cationic compound that has been proposed for use as a fixative for anionic  
30 starch in the wet-end of a papermaking process can be used. Examples include alum, cationic starch or derivatives thereof, polyaluminum compounds, and cationic polymers, such as polydimethyldiallylammonium chlorides, polyamines, polyvinylamines, polyethylene imines, dicyandiamide  
35 polycondensates, or other high molecular weight cationic polymers or copolymers, e.g. comprising a quaternized

nitrogen atom or polyvinyl alcohol, and combinations thereof. Such cationic polymers preferably should have a weight average molecular weight of at least about 10,000, preferably at least about 50,000, more preferably at least 100,000. In a preferred embodiment, the cationic polymers have a weight average molecular weight in the range from about 50,000 to about 2,000,000.

Preferably, a fixative having a high charge density is used. In this regard, a charge density higher than 1  $\mu\text{eq}/\text{mg}$ . is considered a high charge density. The charge density of the fixative is defined as the amount of an anionic polymer (sodium polystyrenesulfonate, Aldrich cat. no. 24,305-1) which has to be added to a known amount of fixative (typically a few milliliters of the fixative in 500 ml demineralized water) in order to reach the equivalence point. This equivalence point may be determined by measuring the electrophoretic zeta potential of the dispersion to which silicate particles are added as indicator. The zeta potential can for instance be measured by using a Malvern Zetasizer 3. It has been found that the use of a fixative having a higher charge density leads to a decreased sensitivity of the papermaking process for the hardness and conductivity of the process water. Preferred fixatives having a high charge density are polyaluminum compounds, such as polyaluminum chloride or polyaluminum sulfate, polydimethyldiallylammonium chlorides, polyamines, and combinations thereof.

In a process for making paper, the anionic starch, which is based on a starch comprising at least 95 wt.%, based on dry substance of the starch, of amylopectin, or a derivative of said starch, and the fixative are added at the wet-end of the process. This means that they are added to a pulp comprising fibers obtained from recycled paper or from wood and water. It is common practice to add a filler compound to the pulp. In accordance with the invention, any of the commonly used filler compounds, such as clay, ground  $\text{CaCO}_3$ , precipitated  $\text{CaCO}_3$ , talc or titaniumdioxide, may be

employed. Preferably, the filler compound is added to the pulp prior to the addition of the anionic starch and the fixative. Further, the anionic starch is preferably added to the pulp before the fixative is added.

5           The amount in which the anionic starch is added to the pulp will depend on the desired paper strength. Generally, the amount will vary between 0.1 and 10 wt.%, preferably between 1 and 5 wt.%, based on (consistency) the weight of the solids in the pulp (fibers, filler compounds,  
10   fines, and so forth).

          The amount of the fixative which is added depends on the nature of the fixative and the pulp that is being used and on the amount of anionic starch that is to be incorporated into the paper. Generally, the amount of  
15   fixative is chosen such that at least 60%, preferably at least 80%, more preferably at least 90% adsorption of the anionic starch is attained. It is noted that in this regard a distinction should be made between adsorption and retention. Retention refers to the amount of starch added in the wet-end  
20   that is eventually incorporated in the paper, while adsorption refers to the amount of starch added in the wet-end that adsorbs to the paper fibers in the pulp in the wet-end. The skilled person will be able to adjust the amount of the fixative to the circumstances at hand. Typical values  
25   differ for inorganic and organic fixatives. When normal, amylose containing anionic starch is used, the weight ratio of fixative to anionic starch is about 1:1 for inorganic fixatives and about 1:4 for organic fixatives. When, in accordance with the invention, an amylopectin type anionic  
30   starch is used, these amounts may be reduced by a factor of about 8-10 for organic fixatives and a factor of about 4-6 for inorganic fixatives.

          The pulp that is used for making paper in a process according to the invention may be any aqueous suspension of  
35   cellulose-based fibers that can be used to make paper from. After the anionic starch and the fixative have been added to

the pulp, the pulp may be processed into paper in any known manner.

The invention will now be further elucidated by the following, non-restrictive examples.

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#### EXAMPLE I

A solution of 30 g urea and 31,1 g phosphoric acid (85%) in 85 ml of water was neutralized to pH 6.0 with 50% NaOH. This solution was mixed with 600 g of amylopectin-potato starch (moisture 20%) for 30 minutes in a Hobart mixer. The mixture was equilibrated and subsequently dried in a Retsch fluid bed dryer for 30 minutes at 60°C, and for 30 minutes at 90°C. the mixture was heated at 145°C in a fluid bed reactor for 30 minutes. The resulting product was HK4017A and had a charge density of 0.47 µeq/mg.

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#### EXAMPLE II

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A solution of 30 g urea and 31,1 g phosphoric acid (85%) in 85 ml of water was neutralized to pH 6.0 with 50% NaOH. This solution was mixed with 600 g of amylopectin-potato starch (moisture 20%) for 30 minutes in a Hobart mixer. The mixture was equilibrated and subsequently dried in a Retsch fluid bed dryer for 30 minutes at 60°C, and for 30 minutes at 90°C. the mixture was heated at 140°C in a fluid bed reactor for 30 minutes. The resulting product was HK4041B and had a charge density of 0.34 µeq/mg.

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#### EXAMPLE III

The adsorption of the starch on to solid pulp components was studied as follows. To a pulp (consistency of 1%) anionic starch was added (dosage 3% on consistency). The pulp was stirred in a baffled beaker at 800 rpm. After 60 seconds a fixative was added and after another 60 seconds the

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pulp was filtered. The starch adsorption was determined by measuring the amount of non-adsorbed starch in the filtrate.

The pulp was a birch sulfate pulp beaten to 35°SR (measured at 21°C) at a consistency of 2% in tap-water using a Hollander. After beating the pulp was diluted to a consistency of 1% with tap-water.

The pulp was divided in three separate batches. The conductivity of one batch was set to 3.01 mS/cm with sodium sulphate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , Merck reinst). The water hardness of the second batch was increased from ca. 11 to ca. 80°GH by adding calcium chloride ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , Merck reinst). The resulting conductivity of this batch was 3.01 mS/cm. To the third batch no salt was added. The conductivity and water hardness was 0.51 mS/cm and ca. 11°GH, respectively. The conductivity of the pulp was measured with a Radiometer CDM 80 conductivity meter.

The starches used are: anionic potato starch PR9510 A (commercialized as Aniofax AP25) and two anionic amylopectin potato starches: HK4017A and HK4041B. The latter two products were prepared as described in Examples I and II, respectively. The starches were cooked with live steam starting with a 10% slurry in tap-water. After cooking the starch solutions were diluted to 5% with hot tap-water. The viscosities of the 5% solutions were determined using a Brookfield LVTDV-II at 60 rpm (see table 1). The degrees of substitution of phosphate in the starches were determined as described in J.Th.L.B. Rameau and J. ten Have, *Chemisch Weekblad*, No. 50 (1951), after excess of phosphate was removed by dialysis against 0.05 N HCl solution for 48 hours and against demineralized water for 24 hours, and neutralization to pH 7-8 with 0.10 N NaOH.

Table 1: Characterization of the applied starches

Starch	DS P [mol/mol]	Viscosity (50°C, 5%) [mPa·s]	pH
PR9510A (AZM)	0.022	391	7.1
HK4017A (AAZM)	0.024	680	7.1
HK4041B (AAZM)	0.018	252	7.2

The used fixatives are Sachtoklar (obtained from Sachtleben Chemie GmbH, Germany), Retinal 1030 (obtained from Joud, France), and PD5-8159 (obtained from Allied Colloids Ltd., UK).

Before use, the fixatives Sachtoklar and Retinal 1030 were diluted by a factor of 10 with demineralized water. A solution of PD5-8159 was prepared by first dissolving 1 g of polymer in 4 g of acetone. After stirring for 30 minutes 95 g demineralized water was added. Some properties of the fixatives are listed in table 2.

The charge density of the fixatives was determined by adding sodium polystyrenesulfonate to a known amount of fixative (typically a few milliliters of the fixative in 500 ml demineralized water). The amount necessary in order to reach the equivalence point was the charge density. This equivalence point was determined by measuring the electrophoretic zeta potential, using a Malvern Zetasizer 3, of the dispersion to which silicate particles were added as indicator.

Table 2: Characterization of the applied fixatives

Fixative	pH of fixative as received	Viscosity (20°C, as received, 60 rpm) [mPa·s]	Solids [%]	Charge density [μeq/mg]
Sachtoklar (= Paper- PAC-N)	2.3	7.3	23.2	+2.0
Retinal 1030	5.7	950	50.1	+7.6
PD5-8159	6.6	2240	26.8	+7.0

The amount of starch in the filtrate was determined in an enzymatic method. In accordance with this method, starch is first converted into glucose with an  $\alpha$ -amylase and an amyloglucosidase. Subsequently, the amount of glucose is determined spectroscopically using a hexokinase test method (Boehringer no. 716251). The amount of starch is calculated from the obtained amount of glucose using a correction factor for incomplete conversion of the starch into glucose by the enzymes. The applied enzymatic conversion factor of Aniofax AP25 is 0.78. The starch adsorption was calculated from the enzymatically determined starch concentration in the filtrate using the following expression:

$$A = 1 - \frac{c_s \times V}{G} \quad \text{eq. A}$$

where  $A$  is the starch adsorption,  $c_s$  is the starch concentration in the filtrate,  $V$  is the total volume of water and  $G$  is the added amount of starch. The total amount of water is obtained by:

$$V = V_p - ds_p + V_{st} - ds_{st} + V_{fix} - ds_{fix} \quad \text{eq. B}$$

where  $V_p$ ,  $V_{st}$  and  $V_{fix}$  represent the volume of the batch of pulp, the volume of the starch dosage and the volume of the fixative dosage, respectively. The total volume is corrected for the dry solids contents  $ds_p$ ,  $ds_{st}$  and  $ds_{fix}$  (assuming density of dry solids is 1 g/ml).

The starch adsorption was investigated by varying three parameters: starch, fixative and pulp properties (conductivity and water hardness). The results will be discussed using the fixative dosage expressed as dry on fiber.



An overview of the fixative dosages needed for a starch adsorption of at least 90% is given in table 3 for each starch and each experimental condition.

The smallest amount of fixative for a starch adsorption >90% is needed in case of HK4017A. For PD5-8159 the fixative dosage is 1.5 to 2.5 times larger in case of HK4041B and 2.5 to 5 times for PR9510A. For Retinal 1030 the increase of the dosage is a factor 2 to 2.5 for HK4041B and 2 to at least 5 for PR9510A.

Also for the PAC Sachtoklar the best results are obtained for the amylopectin starches. In case of PR9510A the PAC dosage is 1.5 to more than 3.5 times higher than in case of HK4017A.

A noteworthy difference between PR9510A and HK4017A is the effectivity of the organic fixatives PD5-8159 and Retinal 1030 at high water hardness. With HK4017A the starch adsorption is higher at high hardness for both fixatives, while with PR9510A the adsorption is the same or lower. Thus, with this anionic AAZM a high water hardness leads to higher starch adsorptions, not only for PACs but also for the tested organic fixatives. In case of the other anionic AAZM, HK4041B, the same effect of water hardness is observed for Retinal 1030, but not for PD5-8159.

These results confirm that the applied organic fixatives are more effective in adsorbing amylopectin molecules than in adsorbing amylose molecules.

**Table 3:** Data for comparison of the starches. The listed fixative dosage is the lowest dosage for which a starch adsorption higher than 90% is obtained. The ratio of fixative dosages is the amount of fixative needed with HK4041B or PR9510A divided by the amount needed for HK4017A.

Exp. nr.	Fixative	Cond. (mS/cm)	Hardness	Starch	Fix. dos.	Starch ads.	Ratio of fix. dos.
1	Sachtoklar	0.51	11	HK4017A	0.46	99.0	-
2	Sachtoklar	0.51	11	HK4041B	0.46	92.6	1
3	Sachtoklar	0.51	11	PR9510A	0.70	98.6	1.5
4	Sachtoklar	3.01	11	HK4017A	0.46	93.4	-
5	Sachtoklar	3.01	11	HK4041B	0.70	90.6	1.5
6	Sachtoklar	3.01	11	PR9510A	1.62	85.6	>3.5
7	Sachtoklar	2.98	80	HK4017A	0.23	95.0	-
8	Sachtoklar	2.98	80	HK4041B	0.46	96.9	2
9	Sachtoklar	2.98	80	PR9510A	0.46	92.6	2
10	PD5-8159	0.51	11	HK4017A	0.10	94.5	-
11	PD5-8159	0.51	11	HK4041B	0.15	92.6	1.5
12	PD5-8159	0.51	11	PR9510A	0.25	92.3	2.5
13	PD5-8159	3.01	11	HK4017A	0.25	98.0	-
14	PD5-8159	3.01	11	HK4041B	0.50	91.9	2
15	PD5-8159	3.01	11	PR9510A	1.00	91.3	4
16	PD5-8159	2.98	80	HK4017A	0.10	97.0	-
17	PD5-8159	2.98	80	HK4041B	0.25	91.7	2.5
18	PD5-8159	2.98	80	PR9510A	0.50	94.2	5
19	Retinal 1030	0.51	11	HK4017A	0.13	95.2	-
20	Retinal 1030	0.51	11	HK4041B	0.25	97.2	2
21	Retinal 1030	0.51	11	PR9510A	0.25	91.8	2
22	Retinal 1030	3.01	11	HK4017A	0.25	92.0	-
23	Retinal 1030	3.01	11	HK4041B	1.00	94.6	4
24	Retinal 1030	3.01	11	PR9510A	1.00	89.9	>4
25	Retinal 1030				2.00	95.7	8
26	Retinal 1030	2.98	80	HK4017A	0.05	90.0	-
27	Retinal 1030	2.98	80	HK4041B	0.13	91.5	2.5
28	Retinal 1030	2.98	80	PR9510A	0.25	93.3	5

Claims

1. A process for making paper wherein an anionic starch, which is based on a starch comprising at least 95 wt.%, based on dry substance of the starch, of amylopectin, or a derivative of said starch, is used in combination with a fixative as a strengthening agent.
2. A process according to claim 1, wherein the starch is a root or tuber starch.
3. A process according to claim 2, wherein the starch is a potato or tapioca starch.
4. A process according to any one of claims 1-3, wherein the derivative of the starch is obtained by an etherification or esterification reaction, or a combination thereof.
5. A process according to any one of the preceding claims, wherein the fixative is a cationic compound having a charge density of at least 1  $\mu\text{eq}/\text{mg}$ .
6. A process according to any one of the preceding claims, wherein the fixative is chosen from the group of polyaluminum compounds, alum, cationic starch or a derivative thereof, polydimethyldiallylammonium chlorides, polyamines, polyvinylamines, polyethylene imines, and dicyandiamide polycondensates.
7. Paper obtainable by a process according to any one of the preceding claims.
8. The use of an anionic starch, which is based on a starch comprising at least 95 wt.%, based on dry substance of the starch, of amylopectin, or a derivative of said starch, as a strengthening agent in paper.
9. The use of an anionic starch, which is based on a starch comprising at least 95 wt.%, based on dry substance of the starch, of amylopectin, or a derivative of said starch, for reducing the amount of a fixative in a process for making paper wherein an anionic starch is used as a strengthening agent.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 99/00351

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 D21H17/28 D21H21/18 D21H23/76

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 282 415 A (ROQUETTE FRERES) 14 September 1988 (1988-09-14) ---	
A	DE 29 24 947 A (GIULINI CHEMIE) 22 January 1981 (1981-01-22) ---	
A	WO 93 01353 A (EKA NOBEL AB) 21 January 1993 (1993-01-21) cited in the application -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

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Date of the actual completion of the international search

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Information on patent family members

International Application No

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